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by

P.L. Roney

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RESEARCH AND DEVELOPMENT BRANCH
DEPARTMENT OF NATIONAL DEFENCE
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ABSTRACT

In this third part of A Theory of Spectral Line Shape for Atmospheric Absorption, an evaluation of the frequency dependence of the complete Fano collision operator has been made using the collision time theory developed earlier. This results in a considerable reduction of the terms in the Fano operator. An analysis of the spectral line wing shows that there are two different regimes: the near wing and the far wing. These regimes are demarcated by a turning point at a frequency displacement of kT/h. In the very far wing, beyond the turning point, the behaviour of the Fano operator changes and the effects of binary collision overlap and photon absorption into the binary collision complex become important. The line wing behaviour is corroborated qualitatively by experimental results for carbon dioxide near 4.2 μm.

RÉSUMÉ

Dans cette troisième partie de notre théorie des profils de raies spectrales, une évaluation de la dépendance par rapport à la fréquence, de l'opérateur de collision de Fano, dans sa totalité, est élaborée grâce à l'application de la théorie de la durée de collision développée antérieurement. Le résultat donne une importante réduction des termes qui composent l'opérateur de Fano. Une analyse de l'aile de la raie spectrale démontre qu'il y a deux régimes différents: l'aile proche du centre et l'aile lointaine. La démarcation entre les deux régimes s'identifie par un point tournant qui se situe à un déplacement en fréquence égal à kT/h. Dans l'aile lointaine, au-delà du point tournant, le comportement de l'opérateur de Fano change et des effets de chevauchement de collisions binaires ainsi que l'absorption d'un photon par le complexe de la collision binaire deviennent importants. Le comportement de l'aile de la raie est confirmé de façon qualitative par des résultats expérimentaux pour le bioxide de carbone dans la région des 4.2 μm.

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EXECUTIVE SUMMARY

The performance of electro-optical sensing devices in both the military and the civilian remote sensing fields can be limited by the propagation characteristics of the atmosphere. It is often assumed that the attenuation by molecular absorption is sufficiently well known for it to be completely predictable. Unfortunately, this is not the case. The two main atmospheric transmission models, LOWTRAN (for broad-band applications) and FASCOD2 (for narrow band and lasers), still have certain limitations.

Recent transmission studies at DREV have revealed that both models deviate from measured transmission in the two main atmospheric transmission windows. One feature which is still modelled inadequately is the absolute transmission of the water vapour continuum over the wide range of temperatures in the troposphere. Another one is the combined carbon dioxide and nitrogen continuum in the 4.2 μm region. A third problem concerns the edges of strong bands of water vapour.

Two of the most important absorption line phenomena, which have not yet been completely described theoretically, are line coupling, or overlap, and the shape of line wings far from the line centres. These phenomena are especially relevant to the above problem areas of LOWTRAN and FASCOD2.

In this third part of the theory of spectral line shapes for infrared atmospheric transmission the problem of the complete wing of an isolated line is examined. The collision time theory, developed in Part II to describe the frequency dependence of line widths and shifts, is applied to the complete Fano operator. Two distinct regions, the near and far wings, having different frequency behaviour are identified. The theoretical line shape is in accord with experimental results for the continuum absorption of carbon dioxide near 4.3 μm.

This work is part of a programme to improve transmission prediction, involving experimental and theoretical studies at DREV and modelling at the Centre for Research in Earth and Space Science, York University.

1.0 INTRODUCTION

The non-Lorentzian nature of the far wings of spectral line shapes is an important phenomenon in the description and modelling of atmospheric transmission. The CO_2 continuum near 4.3 μm and the H_2O vapour continuum, which pervades the atmospheric transmission windows in the 3-5 and 8-12 μm regions, are good examples of the cumulative effects of non-Lorentzian line wings. Fano (Ref. 1) developed an approach to spectral line shape theory whose essential basis was the definition of a collision super operator $m(\omega)$ which is a function of the frequency of the applied radiation field. The diagonal and non-diagonal matrix elements of $m(\omega)$ produce frequency-dependent line widths (and shifts) and coupling parameters, respectively. Various approaches have been used to describe the non-Lorentzian nature of the far wings of lines (Refs. 2-10). Few of these treat directly the composition of the $m(\omega)$ operator as a function of frequency. In some cases, empirical models are used to introduce a collision time as a parameter in the far wing behavior. An exception is Rosenkranz's theory (Ref. 8) and extensions of his theory (Refs. 9,10). This is a statistical theory in which it is assumed that the molecules behave as though they were stationary in the region far from the line centre: the collisions are assumed to have infinite duration. In addition, the distance from the line centre is taken as much greater than the distance between individual lines. Because of these assumptions this theory applies asymptotically to the extreme far line wing. Furthermore, the approximation for the Fano operator results in a band-averaged relaxation parameter which takes into account line coupling without the necessity of calculating the complete set of coupling coefficients.

Until recently, little if any work has been done on the detailed analysis of the frequency dependence of the complete Fano operator. Neither has any attempt been made to perform line shape calculations without first making quite drastic approximations to $m(\omega)$. This is because, apart from the fact that $m(\omega)$ is composed of a formidable number of terms, there existed no simple methods for explicating the frequency dependence of the operator, which is manifested primarily in terms of off-the-energy shell transition operators.

In two recent papers (Refs. 11,12) we have developed an approach to spectral line shape applicable to the conditions for atmospheric infrared transmission. The theory was formulated in Ref. 11 (henceforth referred to as Part I) and was based on a kinetic equation for the density matrix for a system of absorbing molecules in a thermal bath. An iterative solution for the linearized kinetic equation was developed as a density expansion about an isolated line approximation based on Fano's collision operator. The absorption coefficient was determined using linear response theory, together with the fluctuation-dissipation theorem and detailed balance. The isolated line shape has non-Lorentzian wings due to frequency-dependent shift and width parameters, given by the real and imaginary parts, respectively, of the diagonal elements of an averaged $m(\omega)$. New expressions were found for the line coupling terms, dependent on the line strengths of coupled lines as well as the non-diagonal element of $m(\omega)$.

In the second paper (Ref. 12) (henceforth referred to as Part II), formal scattering theory, in the frequency domain, was used to derive a general relation between the off-the-energy shell transition operator (which forms the primary basis of $m(\omega)$) and its on-the-energy shell counterpart. This relation involves a spectral distribution function $\Phi(E,\Delta\omega)$ composed of a complex collision time operator $T(E)$, a time operator $\mathcal{T}(E)$ associated with the free propagator $(E-H_o)^{-1}$, and $\Delta\omega$ the displacement from the line centre. In Part II, this theory was applied only to the near line wing where displacements from the line centre are small compared with the average kinetic energy kT. This condition allowed the retention of only those terms in $m(\omega)$ which are related to the usual impact approximation parameters such as the shift $\Delta(0)$ and width $\Gamma(0)$.

The main objective of this work is to use the collision time theory developed in Part II to carry out an analysis of the contributions of all the terms in the Fano operator to the spectral line wing, including the very far wing region not considered in Part II. We start with a review of the nature of the terms in the Fano operator as discussed by that author. This is followed by a summary of the collision time theory results of Part II. We then apply this theory to each of the terms of the Fano operator and examine the contributions to the near and far line wing.

This work was carried out at DREV between November 1993 and June 1994 under PSC 32E. EO Battlefield Surveillance.

2.0 THE COMPLETE FANO OPERATOR

The original Fano operator $m(\omega)$ was given by eq. 49 of Ref. 1.

$$m(\omega) = t(\omega+H_o^*) - t^*(H_o-\omega) + \frac{1}{2\pi i}\int_{-\infty+i\eta}^{\infty+i\eta} d\psi \left[\frac{1}{\psi-H_o} - \frac{1}{\psi-\omega-H_o^*}\right] t(\psi)\, t^*(\psi-\omega) \left[\frac{1}{\psi-H_o} - \frac{1}{\psi-\omega-H_o^*}\right], \quad [1]$$

where H_o is the interaction-free Hamiltonian and $t(E)$ the transition operator. In Parts I and II we took translational motion into account and in this case we have a thermally averaged operator $M(\Delta\omega)$, where the average is taken over the thermal bath molecules which are assumed to have no interaction with the applied radiation. In the frequency domain the variables are $\Delta\omega_{ab} = (\omega - \omega_{ab})$: the frequency displacement from a line centred at ω_{ab}. After integration over ψ (Ref. 1), the matrix elements of $M(\Delta\omega)$, are represented by

$$M_{acdb}(\Delta\omega) = \langle m_{acdb}(\Delta\omega) \rangle_{AV} = \langle F + \int d\mathbf{k}' \{S + C_1 + P_1 + C_2 + P_2\} \rangle_{AV} \quad [2]$$

where

$$F = t_{aa}(\varepsilon_a+E_k+h\Delta\omega_{ab}) - t^*_{bb}(\varepsilon_b+E_k-h\Delta\omega_{ab}), \quad [3]$$

$$S = +i\pi\, \delta[E_{k'}-E_k-h\Delta\omega_{cb}]\; t_{ac}(\varepsilon_c+E_{k'})\; t^*_{db}(\varepsilon_b+E_k) + i\pi\, \delta[E_{k'}-E_k+h\Delta\omega_{ad}]\; t_{ac}(\varepsilon_a+E_k)\; t^*_{db}(\varepsilon_d+E_{k'}) \quad [4]$$

$$C_1 = +\frac{1}{2}\left\{ - \frac{t_{ac}(\varepsilon_c+E_{k'})\, t^*_{db}(\varepsilon_d+E_{k'}-h\Delta\omega_{cd}) - t_{ac}(\varepsilon_a+E_k)\, t^*_{db}(\varepsilon_b+E_k-h\Delta\omega_{ab})}{E_{k'}-E_k - h\omega_{ac}} + \frac{t_{ac}(\varepsilon_c+E_{k'}+h\Delta\omega_{cd})\, t^*_{db}(\varepsilon_d+E_{k'}) - t_{ac}(\varepsilon_a+E_k+h\Delta\omega_{ab})\, t^*_{db}(\varepsilon_b+E_k)}{E_{k'}-E_k + h\omega_{db}} \right\} \quad [5]$$

$$P_1 = +\frac{1}{2}\left\{ P\frac{t_{ac}(\varepsilon_c+E_{k'})\,t^*_{db}(\varepsilon_d+E_{k'}-h\Delta\omega_{cd})+t_{ac}(\varepsilon_a+E_k+h\Delta\omega_{ab})\,t^*_{db}(\varepsilon_b+E_k)}{E_{k'}-E_k-h\Delta\omega_{cb}} \right.$$

$$\left. - P\frac{t_{ac}(\varepsilon_c+E_{k'}+h\Delta\omega_{cd})\,t^*_{db}(\varepsilon_d+E_{k'})+t_{ac}(\varepsilon_a+E_k)\,t^*_{db}(\varepsilon_b+E_k-h\Delta\omega_{ab})}{E_{k'}-E_k+h\Delta\omega_{ad}} \right\} \quad [6]$$

$$C_2 = +\frac{1}{2\pi i}\int_{-\infty}^{\infty} d\psi\; t_{ac}(\psi+i0)\,t^*_{db}(\psi-\omega-i0)\left[\frac{1}{E_{k'}-E_k-h\omega_{ac}}\left(\frac{P}{\psi-\varepsilon_c-E_{k'}}-\frac{P}{\psi-\varepsilon_a-E_k}\right)\right.$$

$$\left. +\frac{1}{E_{k'}-E_k+h\omega_{db}}\left(\frac{P}{\psi-\varepsilon_c-E_{k'}-h\Delta\omega_{cd}}-\frac{P}{\psi-\varepsilon_a-E_k-h\Delta\omega_{ab}}\right)\right] \quad [7]$$

$$P_2 = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} d\psi\; t_{ac}(\psi+i0)\,t^*_{db}(\psi-\omega-i0)\left[\frac{1}{E_{k'}-E_k-h\Delta\omega_{cb}}\left(\frac{P}{\psi-\varepsilon_c-E_{k'}}-\frac{P}{\psi-\varepsilon_a-E_k-h\Delta\omega_{ab}}\right)\right.$$

$$\left. +\frac{1}{E_{k'}-E_k+h\Delta\omega_{ad}}\left(\frac{P}{\psi-\varepsilon_c-E_{k'}-h\Delta\omega_{cd}}-\frac{P}{\psi-\varepsilon_a-E_k}\right)\right]. \quad [8]$$

Here, E_k is the translational energy and ε_a is the internal energy of the absorber molecules. This corresponds to Fano's well-known eq. 55 with slightly different ordering of the terms†. For brevity, we have temporarily omitted the momentum labelling $\mathbf{k}$ of the t matrices.

In the preceding paper, Part II, a reduced Fano operator was used consisting only of

$$M_{acdb}(\Delta\omega) \propto < F + \int d\mathbf{k}'\, S >_{AV} .$$

This form is valid in the near wing when $\Delta\omega$ is small. As pointed out by Fano (Ref. 1), the remaining terms C_1, C_2, P_1 and P_2 depend on transition matrix elements evaluated off-the-energy shell. In the above form, the off-shell excursions are composed of energy increments $\pm h\Delta\omega_{ab}$ and $\pm h\Delta\omega_{cd}$. When these are negligibly small, as in the impact approximation and in the near line wing, these terms vanish. Fano attributed these terms to the effects of transient stages of collisions, as opposed to the terms F and S which relate

† C_2 and P_2 are twice Fano's due to a misprint in Fano's eq. 55a.

to completed or well-separated collisions. The implication is that the transient effects arise from long collision times so that a collision is not completed before the start of another one. We can expect these transient effects terms to become important in the very far line wing. A major task in this paper is the determination of these terms using the collision time theory developed in Part II.

3.0 SUMMARY OF COLLISION TIME THEORY

In Part II we derived, through formal scattering theory, operator expressions relating off-the-energy shell transition operators to their on-shell values. Thus we showed that

$$t(E+\Delta E+i0) = t(E+i0)\ \Phi(E,\Delta E), \qquad [9]$$

where the spectral distribution operator $\Phi(E,\Delta E)$ is given in terms of two time operators $T(E)$ and $\mathcal{T}(E)$ by the relation

$$\Phi(E,\Delta E) = \left(1 - i\Delta E\ \mathcal{T}(E)/h\right)\left(1 - i\Delta E\ [T(E)+\mathcal{T}(E)]/h\right)^{-1}. \qquad [10]$$

The argument ΔE corresponds to the energy increment off-the-energy shell. In the spectral line application $\Delta E = h\Delta\omega$, and the on-shell energy will correspond to half-shell arguments as in eq. 2. The complex collision time operator $T(E)$ is defined by

$$T(E) = \underset{\eta\to 0}{\mathrm{Lt}}\ \frac{ih}{(E- H_o+i\eta)^2}\ t(E+i\eta) \qquad [11]$$

and the other time operator $\mathcal{T}(E)$ is associated with the free pair propagator $(E-H_o)^{-1}$ by the expression

$$\mathcal{T}(E) = \underset{\eta\to 0}{\mathrm{Lt}}\ \frac{ih}{(E- H_o+i\eta)} \qquad [12]$$

Another convenient form for Φ is

$$\Phi(E,\Delta E) = 1 + (i\Delta E/h)\,T(E)\ \frac{1}{1 - i(\Delta E/h)\,\bar{T}(E)} \qquad [10a]$$

where $$\bar{T}(E) = T(E) + \mathcal{T}(E) \qquad [13]$$

The function $\Phi(E,\Delta E)$ is a spectral distribution function for the energy increment ΔE which compares the total time $\bar{T}(E)$ the molecular pair spend in each other's vicinity during collision with the time $\mathcal{T}(E)$ they would have spent in the interaction vicinity in the absence of the collisional interaction. The asymptotic limit of $\Phi(E,\Delta E)$, as ΔE tends to infinity, is

$$\lim_{\Delta E\to\infty} \Phi(E,\Delta E) = \mathcal{T}(E)\ [T(E)+\mathcal{T}(E)]^{-1}. \qquad [10b]$$

4.0 APPLICATION OF COLLISION TIME THEORY TO THE COMPLETE FANO OPERATOR

In order to evaluate $M(\Delta\omega)$ we will make one simplifying assumption. In accordance with the first order perturbation solution for Φ of Part II, only the diagonal matrix elements of the operators $T(E)$ and $\mathcal{T}(E)$ are retained. Also, since they will always be on an energy shell, we will drop the E argument and merely write $\Phi(\Delta E)$.

We are now in a position to calculate all the terms of eq. 2. Using eq. 9 the forward scattering terms F (eq. 3) are given by

$$F = t_{aa}(\varepsilon_a+E_k+h\Delta\omega_{ab}) - t^*_{bb}(\varepsilon_b+E_k-h\Delta\omega_{ab})$$

$$= t_{aa}(\varepsilon_a+E_k)\Phi_a(\Delta\omega_{ab}) - t^*_{bb}(\varepsilon_b+E_k)\ \Phi^*_b(-\Delta\omega_{ab}) \qquad [14]$$

Similarly, the singular terms S of eq. 4 can be written

$$S = +i\pi\ \delta[E_{k'}-E_k-h\Delta\omega_{cb}]\ t_{ac}(\varepsilon_c+E_{k'})\ t^*_{db}(\varepsilon_b+E_k)$$

$$+i\pi\ \delta[E_{k'}-E_k+h\Delta\omega_{ad}]\ t_{ac}(\varepsilon_a+E_k)\ t^*_{db}(\varepsilon_d+E_{k'})$$

$$= +i\pi\ \delta[E_{k'}-E_k-h\Delta\omega_{cb}]\ t_{ac}(\varepsilon_a+E_k+h\Delta w_{ab})\ t^*_{db}(\varepsilon_b+E_k)$$

$$+i\pi\ \delta[E_{k'}-E_k+h\Delta\omega_{ad}]\ t_{ac}(\varepsilon_a+E_k)\ t^*_{db}(\varepsilon_b+E_k-h\Delta\omega_{ab})$$

$$= i\pi\Big(\delta[E_{k'}-E_k-h\Delta\omega_{cb}]\Phi_a(\Delta\omega_{ab})$$

$$+\ \delta[E_{k'}-E_k+h\Delta\omega_{ad}]\Phi^*_b(-\Delta\omega_{ab})\Big)\, t_{ac}(\varepsilon_a+E_k)\, t^*_{db}(\varepsilon_b+E_k)\ . \qquad [15]$$

Next, the C_1 terms of eq. 5 can be expressed as follows:

$$C_1 = \frac{1}{2}\left\{ - \frac{t_{ac}(\varepsilon_c+E_{k'})\,t^*_{db}(\varepsilon_d+E_{k'}+h\omega_{cd}-h\omega) - t_{ac}(\varepsilon_a+E_k)\,t^*_{db}(\varepsilon_b+E_k-h\Delta\omega)}{E_{k'}-E_k-h\omega_{ac}} \right.$$

$$\left. + \frac{t_{ac}(\varepsilon_c+E_{k'}+h\omega-h\omega_{cd})\,t^*_{db}(\varepsilon_d+E_{k'}) - t_{ac}(\varepsilon_a+E_k+h\Delta\omega)\,t^*_{db}(\varepsilon_b+E_k)}{E_{k'}-E_k+h\omega_{db}} \right\}$$

$$= \frac{1}{2}\left\{ t_{ac}(\varepsilon_a+E_k)\,t^*_{db}(\varepsilon_b+E_k) \left[\frac{\Phi^*_b(-\Delta\omega_{ab})}{E_{k'}-E_k-h\omega_{ac}} - \frac{\Phi_a(\Delta\omega_{ab})}{E_{k'}-E_k+h\omega_{db}} \right] \right.$$

$$\left. - t_{ac}(\varepsilon_c+E_{k'})\,t^*_{db}(\varepsilon_d+E_{k'}) \left[\frac{\Phi^*_d(-\Delta\omega_{cd})}{E_{k'}-E_k-h\omega_{ac}} - \frac{\Phi_c(\Delta\omega_{cd})}{E_{k'}-E_k+h\omega_{db}} \right] \right\}. \qquad [16]$$

For the first set of principal value terms P_1 (eq. 6) we write the off-shell t elements in terms of on-shell elements (using eq. 9):

$$P_1 = \frac{1}{2}\left\{ P\,\frac{t_{ac}(\varepsilon_c+E_{k'})\,t^*_{db}(\varepsilon_d+E_{k'})\,\Phi^*_d(-\Delta\omega_{cd}) + t_{ac}(\varepsilon_a+E_k)\,t^*_{db}(\varepsilon_b+E_k)\,\Phi_a(\Delta\omega_{ab})}{E_{k'}-E_k-h\Delta\omega_{cb}} \right.$$

$$\left. - P\,\frac{t_{ac}(\varepsilon_c+E_{k'})\,t^*_{db}(\varepsilon_d+E_{k'})\,\Phi_c(\Delta\omega_{cd}) + t_{ac}(\varepsilon_a+E_k)\,t^*_{db}(\varepsilon_b+E_k)\,\Phi^*_b(-\Delta\omega_{ab})}{E_{k'}-E_k+h\Delta\omega_{ad}} \right\}$$

$$= \frac{1}{2}\left\{ t_{ac}(\varepsilon_c+E_{k'})\,t^*_{db}(\varepsilon_d+E_{k'}) \left[\frac{\Phi^*_d(-\Delta\omega_{cd})}{E_{k'}-E_k-h\Delta\omega_{cb}} - \frac{\Phi_c(\Delta\omega_{cd})}{E_{k'}-E_k+h\Delta\omega_{ad}} \right] \right.$$

$$\left. - t_{ac}(\varepsilon_a+E_k)\,t^*_{db}(\varepsilon_b+E_k) \left[\frac{\Phi^*_b(-\Delta\omega_{ab})}{E_{k'}-E_k+h\Delta\omega_{ad}} - \frac{\Phi_a(\Delta\omega_{ab})}{E_{k'}-E_k-h\Delta\omega_{cb}} \right] \right\}. \qquad [17]$$

In the last set of terms, C_2 (eq. 7) and P_2 (eq. 8), we first use eq. 9 to write the t matrices in terms of their appropriate on-shell counterparts. At this point we can identify four integrals over the variable ψ and write C_2 and P_2 in the following form:

$$C_2 = \frac{1}{2}\left\{ t_{ac}(\varepsilon_c + E_{k'})\, t^*_{db}(\varepsilon_d + E_{k'}) \left[\frac{I_1}{E_{k'}-E_k-h\omega_{ac}} + \frac{I_3}{E_{k'}-E_k+h\omega_{db}} \right] \right.$$

$$\left. - t_{ac}(\varepsilon_a + E_k)\, t^*_{db}(\varepsilon_b + E_k) \left[\frac{I_2}{E_{k'}-E_k-h\omega_{ac}} + \frac{I_4}{E_{k'}-E_k+h\omega_{db}} \right] \right\} , \qquad [18]$$

$$P_2 = -\frac{1}{2}\left\{ t_{ac}(\varepsilon_c + E_{k'})\, t^*_{db}(\varepsilon_d + E_{k'}) \left[\frac{I_1}{E_{k'}-E_k-h\Delta\omega_{cb}} + \frac{I_3}{E_{k'}-E_k+h\Delta\omega_{ad}} \right] \right.$$

$$\left. - t_{ac}(\varepsilon_a + E_k)\, t^*_{db}(\varepsilon_b + E_k) \left[\frac{I_4}{E_{k'}-E_k-h\Delta\omega_{cb}} + \frac{I_2}{E_{k'}-E_k+h\Delta\omega_{ad}} \right] \right\} , \qquad [19]$$

where the four integrals I_1, I_2, I_3 and I_4 are all of the same type and are evaluated in Appendix A:

$$I_1 = \frac{1}{\pi i}\int_{-\infty}^{\infty} d\psi \; \frac{P}{\psi-\varepsilon_c-E_{k'}}\, \Phi_c(\psi-\varepsilon_c-E_{k'})\; \Phi^*_d(\psi-\varepsilon_d-E_{k'},-h\Delta\omega_{cd})$$

$$= 2\Theta_{cd}(\Delta\omega_{cd}) + \Phi^*_d(-\Delta\omega_{cd}) , \qquad [20a]$$

$$I_2 = \frac{1}{\pi i}\int_{-\infty}^{\infty} d\psi \; \frac{P}{\psi-\varepsilon_a-E_k}\, \Phi_a(\psi-\varepsilon_a-E_k)\; \Phi^*_b(\psi-\varepsilon_a-E_k-h\Delta\omega_{ab})$$

$$= 2\Theta_{cd}(\Delta\omega_{ab}) + \Phi^*_b(-\Delta\omega_{ab}) , \qquad [20b]$$

$$I_3 = \frac{1}{\pi i}\int_{-\infty}^{\infty} d\psi \; \frac{P}{\psi-\varepsilon_c-E_{k'},-h\Delta\omega_{cd}}\, \Phi_c(\psi-\varepsilon_c-E_{k'})\; \Phi^*_d(\psi-\varepsilon_d-E_{k'},-h\Delta\omega_{cd})$$

$$= -\left[2\Psi_{cd}(\Delta\omega_{cd}) + \Phi_c(\Delta\omega_{cd})\right] , \qquad [20c]$$

$$I_4 = \frac{1}{\pi i}\int_{-\infty}^{\infty} d\psi \; \frac{P}{\psi-\varepsilon_a-E_k-h\Delta\omega_{ab}}\, \Phi_c(\psi-\varepsilon_a-E_k)\; \Phi^*_d(\psi-\varepsilon_a-E_k-h\Delta\omega_{ab})$$

$$= -\left[2\Psi_{cd}(\Delta\omega_{ab}) + \Phi_a(\Delta\omega_{ab})\right] \qquad [20d]$$

The new spectral distributions appearing in eq. 20 are:

$$\Theta_{cd}(\Delta\omega_{cd}) = (1+T_c/\bar{T}_c)(1-T_d^*/\bar{T}_d^*)/2 + \frac{(T_c T_d^*/\bar{T}_d^*)}{(\bar{T}_d^*+\bar{T}_c)-i\bar{T}_c\bar{T}_d^*\Delta\omega_{cd}} - \Phi_d^*(-\Delta\omega_{cd}) \quad [21]$$

$$\Psi_{cd}(\Delta\omega_{cd}) = (1-T_c/\bar{T}_c)(1+T_d^*/\bar{T}_d^*)/2 + \frac{(T_c T_d^*/\bar{T}_c)}{(\bar{T}_d^*+\bar{T}_c)-i\bar{T}_c\bar{T}_d^*\Delta\omega_{cd}} - \Phi_c(\Delta\omega_{cd}). \quad [22]$$

It is important to note the different nature of these functions compared with $\Phi_c(\Delta\omega_{cd})$ and $\Phi_d^*(-\Delta\omega_{cd})$. Both $\Theta_{cd}(\Delta\omega_{cd})$ and $\Psi_{cd}(\Delta\omega_{cd})$ are mixed functions of the collision times T_c, $\bar{T}_c$, T_d^* and $\bar{T}_d^*$: it is not possible to reduce these into separate parts dependent on the collision time pairs T_c, $\bar{T}_c$ and T_d^*, $\bar{T}_d^*$ alone, as in $\Phi_c(\Delta\omega_{cd})$ and $\Phi_d^*(-\Delta\omega_{cd})$. Terms containing functions $\Theta_{cd}(\Delta\omega_{cd})$ and $\Psi_{cd}(\Delta\omega_{cd})$ therefore refer to overlapping binary collisions since it is not possible to distinguish between each binary collision through its time of duration. This is in accord with Fano's reference to transient effects (Ref. 1) arising from collisions which cannot be regarded as entirely isolated events.

The asymptotic limits for the different spectral distribution functions, as $\Delta\omega_{cd}$ tends to infinity, are important:

$$\lim_{\Delta\omega\to\infty} \Phi_c(\Delta\omega) = (\mathcal{T}_c/\bar{T}_c) \ , \quad [10c]$$

$$\lim_{\Delta\omega\to\infty} \Phi_d^*(-\Delta\omega) = (\mathcal{T}_d^*/\bar{T}_d^*), \quad [10d]$$

$$\lim_{\Delta\omega\to\infty} \Theta_{cd}(\Delta\omega) = -(1-T_c/\bar{T}_c)(1-T_d^*/\bar{T}_d^*)/2 = \lim_{\Delta\omega\to\infty} \Psi_{cd}(\Delta\omega) \quad [21a]$$

Substituting for eq. 20 in eqs. 18 and 19, and collecting and regrouping the terms C_1 and C_2 (eqs. 16 and 18) and P_1 and P_2 (eqs. 17 and 19) we can write

$$C = C_1 + C_2 = \frac{1}{2}\left\{ - t_{ac}(\varepsilon_c+E_{k'})\,t_{db}^*(\varepsilon_d+E_{k'}) \left[\frac{\Phi_d^*(-\Delta\omega_{cd})-I_1}{E_{k'}-E_k-h\omega_{ac}} - \frac{\Phi_c(\Delta\omega_{cd})+I_3}{E_{k'}-E_k+h\omega_{db}} \right] \right.$$

$$\left. + t_{ac}(\varepsilon_a+E_k)\,t_{db}^*(\varepsilon_b+E_k) \left[\frac{\Phi_b^*(-\Delta\omega_{ab})-I_2}{E_{k'}-E_k-h\omega_{ac}} - \frac{\Phi_a(\Delta\omega_{ab})+I_4}{E_{k'}-E_k+h\omega_{db}} \right] \right\}$$

$$= \left\{ t_{ac}(\varepsilon_c+E_{k'})\, t^{*}_{db}(\varepsilon_d+E_{k'}) \left[\frac{\Theta_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k-h\omega_{ac}} - \frac{\Psi_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k+h\omega_{db}} \right] \right.$$

$$\left. - t_{ac}(\varepsilon_a+E_k)\, t^{*}_{db}(\varepsilon_b+E_k) \left[\frac{\Theta_{cd}(\Delta\omega_{ab})}{E_{k'}-E_k-h\omega_{ac}} - \frac{\Psi_{cd}(\Delta\omega_{ab})}{E_{k'}-E_k+h\omega_{db}} \right] \right\}, \qquad [23]$$

$$P = P_1 + P_2 = \frac{1}{2} \left\{ t_{ac}(\varepsilon_c+E_{k'})\, t^{*}_{db}(\varepsilon_d+E_{k'}) \left[\frac{-\Phi_c(\Delta\omega_{cd})-I_3}{E_{k'}-E_k+h\Delta\omega_{ad}} + \frac{\Phi^{*}_d(-\Delta\omega_{cd})-I_1}{E_{k'}-E_k-h\Delta\omega_{cb}} \right] \right.$$

$$\left. - t_{ac}(\varepsilon_a+E_k)\, t^{*}_{db}(\varepsilon_b+E_k) \left[\frac{\Phi^{*}_b(-\Delta\omega_{ab})-I_2}{E_{k'}-E_k+h\Delta\omega_{ad}} - \frac{\Phi_a(\Delta\omega_{ab})+I_4}{E_{k'}-E_k-h\Delta\omega_{cb}} \right] \right\}$$

$$= \left\{ t_{ac}(\varepsilon_c+E_{k'})\, t^{*}_{db}(\varepsilon_d+E_{k'}) \left[\frac{\Psi_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k+h\Delta\omega_{ad}} - \frac{\Theta_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k-h\Delta\omega_{cb}} \right] \right.$$

$$\left. + t_{ac}(\varepsilon_a+E_k)\, t^{*}_{db}(\varepsilon_b+E_k) \left[\frac{\Theta_{cd}(\Delta\omega_{ab})}{E_{k'}-E_k+h\Delta\omega_{ad}} - \frac{\Psi_{cd}(\Delta\omega_{ab})}{E_{k'}-E_k-h\Delta\omega_{cb}} \right] \right\}. \qquad [24]$$

Substituting in eq. 2 for the terms F, S, C and P from eqs. 3, 4, 23 and 24, respectively, taking the thermal average over the reservoir molecules and re-introducing the momentum labelling for the transition matrices, we obtain the matrix elements of $M(\Delta\omega)$

$$M_{acdb}(\Delta\omega) = \langle F + \int d\mathbf{k}' \{S + C_1 + P_1 + C_2 + P_2\} \rangle_{AV}$$

$$= \mathrm{Tr}_2 \int d\mathbf{k}\; f_2^{eq}(\mathbf{k})$$

$$\times \left\{ \langle \mathbf{k} | t_{aa}(\varepsilon_a+E_k) | \mathbf{k} \rangle\, \Phi_a(\Delta\omega_{ab})\, \delta_{db} - \langle \mathbf{k} | t^{*}_{bb}(\varepsilon_b+E_k) | \mathbf{k} \rangle\, \Phi^{*}_b(-\Delta\omega_{ab})\, \delta_{ca} \right.$$

$$+ \int d\mathbf{k}' \left[\pi i\, \langle \mathbf{k} | t_{ac}(\varepsilon_a+E_k) | \mathbf{k}' \rangle \langle \mathbf{k}' | t^{*}_{db}(\varepsilon_b+E_k) | \mathbf{k} \rangle \right.$$

$$\left. \left. \times \left(\delta[E_{k'}-E_k-h\Delta\omega_{cb}]\, \Phi_a(\Delta\omega_{ab}) + \delta[E_{k'}-E_k+h\Delta\omega_{ad}]\, \Phi^{*}_b(-\Delta\omega_{ab}) \right) \right.\right.$$

$$+ \langle \mathbf{k} | t_{ac}(\varepsilon_a + E_{k'}) | \mathbf{k}' \rangle \langle \mathbf{k}' | t^*_{db}(\varepsilon_b + E_{k'}) | \mathbf{k} \rangle \left(\frac{\Theta_{cd}(\Delta\omega_{cd})}{E_{k'} - E_k - h\omega_{ac}} - \frac{\Psi_{cd}(\Delta\omega_{cd})}{E_{k'} - E_k + h\omega_{db}} \right)$$

$$- \langle \mathbf{k} | t_{ac}(\varepsilon_c + E_k) | \mathbf{k}' \rangle \langle \mathbf{k}' | t^*_{db}(\varepsilon_d + E_k) | \mathbf{k} \rangle \left(\frac{\Theta_{cd}(\Delta\omega_{ab})}{E_{k'} - E_k - h\omega_{ac}} - \frac{\Psi_{cd}(\Delta\omega_{ab})}{E_{k'} - E_k + h\omega_{db}} \right)$$

$$+ \langle \mathbf{k} | t_{ac}(\varepsilon_a + E_{k'}) | \mathbf{k}' \rangle \langle \mathbf{k}' | t^*_{db}(\varepsilon_b + E_{k'}) | \mathbf{k} \rangle \left(\frac{\Psi_{cd}(\Delta\omega_{cd})}{E_{k'} - E_k + h\Delta\omega_{ad}} - \frac{\Theta_{cd}(\Delta\omega_{cd})}{E_{k'} - E_k - h\Delta\omega_{cb}} \right)$$

$$+ \langle \mathbf{k} | t_{ac}(\varepsilon_a + E_k) | \mathbf{k}' \rangle \langle \mathbf{k}' | t^*_{db}(\varepsilon_b + E_k) | \mathbf{k} \rangle \left(\frac{\Theta_{cd}(\Delta\omega_{ab})}{E_{k'} - E_k + h\Delta\omega_{ad}} - \frac{\Psi_{cd}(\Delta\omega_{ab})}{E_{k'} - E_k - h\Delta\omega_{cb}} \right) \Bigg] \Bigg\} . \quad [25]$$

The *C* and *P* terms of eq. 25 (i.e. the last four terms) still contain off-shell transition matrices (energy argument is $E_{k'}$ rather than E_k) as well as on-shell matrices. These off-shell transition matrices can be expressed in terms of the corresponding on-shell matrices. The two are connected by delay time operators. These delay times are well known, especially through the work of Felix Smith (Ref. 13). They are present in all collisions, even binary ones, and are not dependent on the intervention of a third body. The delay times express the fact that, in a binary collision for example, the colliding pair travels for a time as a quasi-bound state similar to a dimer, before finally separating. The delay time is a measure of the difference in time spent in collision compared with the time over the same trajectory in the absence of the interaction. It can be positive or negative, depending on whether the interaction is attractive or repulsive. It is therefore to be expected that this type of kinematic effect will appear in the *C* and *P* terms which are associated with collisional overlap. We will use the delay time theory to account for this effect to first order approximation.

The delay time Δt is defined in terms of the energy derivative of the phase shift η

$$\Delta t = 2\hbar \, \partial\eta / \partial E. \quad [26]$$

The first order approximation for the off-shell t-matrix products of eq. 25 can be obtained by a Taylor series expansion about the on-shell energies:

$$\langle \mathbf{k}|\, t_{aa}(\varepsilon_a+E_{k'})\,|\mathbf{k}'\rangle\langle \mathbf{k}'|\, t^{*}_{bb}(\varepsilon_b+E_{k'})\,|\mathbf{k}\rangle \simeq \langle \mathbf{k}|\, t_{aa}(\varepsilon_a+E_{k})\,|\mathbf{k}'\rangle\langle \mathbf{k}'|\, t^{*}_{bb}(\varepsilon_b+E_{k})\,|\mathbf{k}\rangle$$

$$+ (E_{k'}-E_k)\,\frac{\partial}{\partial E_{k'}}\Big(\langle \mathbf{k}|\, t_{aa}(\varepsilon_a+E_{k})\,|\mathbf{k}'\rangle\Big)\langle \mathbf{k}'|\, t^{*}_{bb}(\varepsilon_b+E_{k})\,|\mathbf{k}\rangle$$

$$+ (E_{k'}-E_k)\,\langle \mathbf{k}|\, t_{aa}(\varepsilon_a+E_{k})\,|\mathbf{k}'\rangle\,\frac{\partial}{\partial E_{k'}}\Big(\langle \mathbf{k}'|\, t^{*}_{bb}(\varepsilon_b+E_{k})\,|\mathbf{k}\rangle\Big). \qquad [27]$$

The next step is to write the transition matrix elements in terms of the phase shift. The phase shift is complex because we are dealing with inelastic collisions in the terms C and P. For example, assuming spherical symmetry for simplicity, and dropping the internal state labels for the same reason, partial wave analysis leads to

$$\langle \mathbf{k}|\, t\ (E_{k'})\,|\mathbf{k}'\rangle = -(2\pi/m)\ f(\theta) = \frac{i\pi}{mk}\sum_{l}(2l+1)(e^{2i\eta_l}-1)\ P_l(\cos\theta), \qquad [28]$$

and

$$\frac{\partial}{\partial E_{k'}}\Big(\langle \mathbf{k}|\, t\ (E_{k'})\,|\mathbf{k}'\rangle\Big) = -\frac{\pi}{\hbar mk}\,Q(\theta) = -\frac{\pi}{mk}\,Q(\theta), \qquad [29]$$

where the wavenumber $k = k/\hbar$ and we have defined a delay time

$$Q(\theta) = 2\hbar\sum_{l}(2l+1)\ e^{2i\eta_l}\ (\partial\eta_l/\partial E_{k'})\ P_l(\cos\theta). \qquad [30]$$

It follows from eqs. 26-30 that, in general, we can write the approximation

$$\langle \mathbf{k}|\, t_{aa}(\varepsilon_a+E_{k'})\,|\mathbf{k}'\rangle\langle \mathbf{k}'|\, t^{*}_{bb}(\varepsilon_b+E_{k'})\,|\mathbf{k}\rangle$$

$$\simeq \langle \mathbf{k}|\, t_{aa}(\varepsilon_a+E_{k})\,|\mathbf{k}'\rangle\langle \mathbf{k}'|\, t^{*}_{bb}(\varepsilon_b+E_{k})\,|\mathbf{k}\rangle$$

$$+ \frac{2\pi^2\ (E_{k'}-E_k)}{m^2k'}\Big(Q_{aa}(\Omega)\,f^{*}_{bb}(\Omega) + f_{aa}(\Omega)\,Q^{*}_{bb}(\Omega)\Big). \qquad [31]$$

It is now convenient to express all the t matrix elements of eq. 25 in terms of scattering amplitudes $f(\Omega,k')$ and introducing eq. 31 we obtain

$$M_{acdb}(\Delta\omega) = n_2\left\{-\frac{2\pi}{m}\left[\Phi_a(\Delta\omega_{ab})\ f_{aa}(0) - \Phi^{*}_{b}(-\Delta\omega_{ab})\ f^{*}_{bb}(0)\right]\right.$$

$$+\frac{2\pi^2}{m^2}\int d\mathbf{k}'\left[2\pi i\left(\delta[E_{k'}-E_k-h\Delta\omega_{cb}]\Phi_a(\Delta\omega_{ab})+\delta[E_{k'}-E_k+h\Delta\omega_{ad}]\Phi_b^*(-\Delta\omega_{ab})\right)f_{ac}(\Omega)f_{db}^*(\Omega)\right.$$

$$-\left(\frac{\Psi_{cd}(\Delta\omega_{ab})+\Theta_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k-h\Delta\omega_{cb}}-\frac{\Psi_{cd}(\Delta\omega_{cd})+\Theta_{cd}(\Delta\omega_{ab})}{E_{k'}-E_k+h\Delta\omega_{ad}}\right)f_{ac}(\Omega)f_{db}^*(\Omega)$$

$$-\frac{(E_{k'}-E_k)}{2k'}\left(\frac{\Theta_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k-h\Delta\omega_{cb}}-\frac{\Theta_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k-h\omega_{ac}}-\frac{\Psi_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k+h\Delta\omega_{ad}}+\frac{\Psi_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k+h\omega_{db}}\right)$$

$$\left.\left.\times\left(Q_{ac}(\Omega)f_{db}^*(\Omega)+f_{ac}(\Omega)Q_{db}^*(\Omega)\right)\right]\right\}_{AV}, \qquad [32]$$

where n_2 is the number density of the thermal reservoir molecules. In passing, we note the difference between the delay time Q and the collision time operator T (eq. 11). Q, as defined, relates only to a kinematic excursion off the energy shell which affects only the translational energy. It is not directly connected with the intervention of a photon during a binary collision process. T, on the other hand, is defined essentially in terms of a derivative with respect to the whole energy: translational plus internal energy. The fact that the off-shell deviation of $t(E+\Delta E)$ can be expressed in terms of T and $\Delta E = h\Delta w$ (through the spectral distribution functions Φ) is due to the direct interaction of a photon with the absorber's internal states during the collision. We now apply the optical theorem to the forward scattering terms of eq. 32

$$Im\ f(0) = k\,\sigma/4\pi\ , \qquad [33]$$

where σ is the total cross-section. Also, remembering that $\mathbf{k}'$ has the same magnitude as $\mathbf{k}$, but is at angles θ and ϕ to it, we can express the integration over $d\mathbf{k}'$in eq. 32 as one over $dE_{k'}$ Thus,

$$d\mathbf{k}' = mk'\ dE_{k'}\ d\Omega\ /8\pi^3, \qquad [34]$$

where Ω is a solid angle. Equation 32 becomes

$$M_{acdb}(\Delta\omega) = n_2\left\{-\frac{2\pi}{m}\left[\Phi_a(\Delta\omega_{ab})Re\ f_{aa}(0)-\Phi_b^*(-\Delta\omega_{ab})Re\ f_{bb}^*(0)\right]\right.$$

$$- \frac{iv}{2}\left[\Phi_a(\Delta\omega_{ab})\sigma_{aa} + \Phi_b^*(-\Delta\omega_{ab})\sigma_{bb}\right]$$

$$+\frac{1}{2m}\int dE_{k'}\,d\Omega k'\left[i\left(\delta[E_{k'}-E_k-h\Delta\omega_{cb}]\Phi_a(\Delta\omega_{ab})+\delta[E_{k'}-E_k+h\Delta\omega_{ad}]\Phi_b^*(-\Delta\omega_{ab})\right)f_{ac}(\Omega)f_{db}^*(\Omega)\right.$$

$$-\frac{1}{2\pi}\left(\frac{\Psi_{cd}(\Delta\omega_{ab})+\Theta_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k-h\Delta\omega_{cb}}-\frac{\Psi_{cd}(\Delta\omega_{cd})+\Theta_{cd}(\Delta\omega_{ab})}{E_{k'}-E_k+h\Delta\omega_{ad}}\right)f_{ac}(\Omega)f_{db}^*(\Omega)$$

$$-\frac{(E_{k'}-E_k)}{4\pi k'}\left(\frac{\Theta_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k-h\Delta\omega_{cb}}-\frac{\Theta_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k-h\omega_{ac}}-\frac{\Psi_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k+h\Delta\omega_{ad}}+\frac{\Psi_{cd}(\Delta\omega_{cd})}{E_{k'}-E_k+h\omega_{db}}\right)$$

$$\left.\left.\times\left(Q_{ac}(\Omega)f_{db}^*(\Omega)+f_{ac}(\Omega)Q_{db}^*(\Omega)\right)\right]\right\}_{AV}, \qquad [35]$$

Comparing eq. 35 with the original form of Fano's operator (eq. 2 with eqs. 3-8), the collision time theory has permitted a considerable reduction in the number of terms. The terms themselves are also more accessible to physical interpretation and, although still difficult to calculate for specific molecular constituents, their effects on spectral line wings can be discussed fairly readily in analytical terms.

5.0 DIAGONAL ELEMENTS OF THE FANO OPERATOR AND THE LINE WING

For an analysis of the non-Lorentzian wings of isolated spectral lines we are primarily concerned with the diagonal elements $M_{aabb}(\Delta\omega)$. The analysis of the non-diagonal elements, although necessarily more complicated, follows the general lines of the following treatment. Denoting $\Delta\omega_{ab}$ by $\Delta\omega$, the diagonal elements are

$$M_{aabb}(\Delta\omega) = n_2\left\{-\frac{2\pi}{m}\left[\Phi_a(\Delta\omega)Re\,f_{aa}(0) - \Phi_b^*(-\Delta\omega)Re\,f_{bb}^*(0)\right]\right.$$

$$-\frac{iv}{2}\left[\Phi_a(\Delta\omega)\sigma_{aa} + \Phi_b^*(-\Delta\omega)\sigma_{bb}\right]$$

$$+\frac{1}{2m}\int dE_{k'}\,d\Omega\;k'\left[i\left(\delta[E_{k'}-E_k-h\Delta\omega]\Phi_a(\Delta\omega)+\delta[E_{k'}-E_k+h\Delta\omega]\Phi_b^*(-\Delta\omega)\right)f_{aa}(\Omega)f_{bb}^*(\Omega)\right.$$

$$- \frac{1}{2\pi}\left(\Psi_{ab}(\Delta\omega) + \Theta_{ab}(\Delta\omega)\right)\left(\frac{P}{E_{k'}-E_k-h\Delta\omega} - \frac{P}{E_{k'}-E_k+h\Delta\omega}\right) f_{aa}(\Omega) f^*_{bb}(\Omega)$$

$$- \frac{h\Delta\omega}{4\pi k'}\left(\frac{\Theta_{ab}(\Delta\omega)}{E_{k'}-E_k-h\Delta\omega} + \frac{\Psi_{ab}(\Delta\omega)}{E_{k'}-E_k+h\Delta\omega}\right)\left(Q_{aa}(\Omega) f^*_{bb}(\Omega) + f_{aa}(\Omega) Q^*_{bb}(\Omega)\right)\Bigg]\Bigg\}_{AV}. \qquad [36]$$

This result shows a further reduction in terms. In some cases it may even be possible to neglect the last term (which depends basically on $h\Delta\omega Q$) when the delay times are very small. However, the most interesting aspect of eq. 36 is that, because of the factors $[E_{k'}-E_k \pm h\Delta\omega]$, there are two regimes for the diagonal elements $M_{aabb}(\Delta\omega)$, depending on whether $h\Delta\omega$ is much greater or smaller than $E_k \sim k^2/2m$. We shall first examine the case for small $h\Delta\omega << E_k$ which is the near wing region.

5.1 The Near Wing Region

The near wing situation was discussed in Part II and corresponds to the case of $\Delta\omega_{ab} = \omega - \omega_{ab}$ small but finite. More specifically, when $h\Delta\omega_{ab} << k^2/2m \simeq kT$ this factor can be neglected simultaneously in both the delta functions and the denominators of the terms in eq. 36. In this approximation the principal value terms cancel out completely (as indicated by Fano in Ref. 1) and the delay time term is negligible. (In fact, the justification for the dropping of all these terms for small $\Delta\omega$ is more readily evident in eq. 25). The two parts of the singular S term combine under a single delta function $\delta(E_{k'}-E_k)$ and the integration over $E_{k'}$ can be carried out. Finally, the result for the near wing version of eq. 36 can be written

$$M_{aabb}(\Delta\omega) = n_2\left\{\frac{-2\pi}{m}\left[\Phi_a(\Delta\omega)\ Ref_{aa}(0) - \Phi^*_b(-\Delta\omega)\ Ref^*_{bb}(0)\right]\right.$$

$$- \frac{iv}{2}\left[\Phi_a(\Delta\omega)\ \sigma_{aa} + \Phi^*_b(-\Delta\omega)\ \sigma_{bb}\right]$$

$$\left. + \frac{iv}{2}\left[\Phi_a(\Delta\omega_{ab}) + \Phi^*_b(-\Delta\omega_{ab})\right]\int d\Omega\ f_{aa}(\Omega)\ f^*_{bb}(\Omega)\right\}_{AV}, \qquad [37]$$

where v is the average perturber velocity.

An important point feature of this result is that, for the near wing approximation, the frequency dependence of $M_{aabb}(\Delta\omega)$ is determined entirely by the spectral distribution functions Φ. Although we require a knowledge of the pair interaction to calculate the collision time T (in order to determine Φ, eq. 10), the only other interaction information needed is at the impact theory level involving $f(0)$ and $f(\Omega)$. Thus eq. 37 (with eq. 10 for Φ) shows that for the near wing region, the frequency dependence of the real and imaginary parts of $M_{aabb}(\Delta\omega)$ are determined by simple rational functions whose numerators and denominators are quadratic in $\Delta\omega$. The near wing theory was applied to the CO_2 continuum beyond the band head near 4 μm in Part II.

Because the range of validity of the near wing approximation is about 200 cm^{-1} ($\Delta\omega \leq kT/h$) for ambient temperatures, it should be quite accurate for most purposes within an infrared band at low pressures. In such calculations one also needs to take into account the line coupling effects as described in I. The corresponding frequency-dependent non-diagonal elements of $M_{acdb}(\Delta\omega)$, for small $\Delta\omega$, were given in Part II.

5.2 The Far Wing Region

In the far wing region where $h\Delta\omega_{ab} >> E_k$ we cannot make the same approximations as in the near wing region: all the terms of eq. 36 must be retained. Although the spectral distribution functions Φ, Θ and Ψ all play a role in the frequency dependence of $M_{aabb}(\Delta\omega)$, this is also determined by the specifics of the perturber-absorber interaction which affects the singular as well as the principal value terms. However, it is still possible, without going into the details of the interaction, to further elucidate the nature of these terms as we go out further into the line wing. We have already indicated that the nature of the spectral distribution functions Θ and Ψ is such that these correspond to overlapping binary collisions where there is a mixing of the absorber internal states a and b.

We first examine the effects of the delta functions in the singular terms of eq. 36. These consist of S_+ and S_- where

$$S_+ = \frac{i}{2m}\,\Phi_a(\Delta\omega) \iint dE_{k'}\, d\Omega\, k'\, \delta[E_{k'}-E_k-h\Delta\omega]\; f_{aa}(\Omega) f^*_{bb}(\Omega), \qquad [38]$$

$$S_- = \frac{i}{2m}\,\Phi^*_b(-\Delta\omega) \iint dE_{k'}\, d\Omega\, k'\, \delta[E_{k'}-E_k+h\Delta\omega]\; f_{aa}(\Omega) f^*_{bb}(\Omega). \qquad [39]$$

The delta functions give $E_{k'} \rightarrow (E_k \pm h\Delta\omega)$. Now, in the partial wave analysis of collision processes the phase shift is given in terms of the energy as a function of the wave number k. The latter is related to the linear momentum k by

$$k = k/\hbar = (2mE)^{1/2}/\hbar\ .$$

We first assume that $\Delta\omega$ is positive so that we are looking at the high frequency wing. If $h\Delta\omega >> k^2/2m$ then $E_{k'} \rightarrow (E_k \pm h\Delta\omega)$ means

$$k' \rightarrow [\ 2m\ (k^2/2m + h\Delta\omega\ )\ ]^{1/2}\ /\hbar = \hbar^{-1}(2mh\Delta\omega)^{1/2}\left(1 + \frac{k^2}{2mh\Delta\omega}\right)^{1/2} \qquad [40a]$$

and

$$k' \rightarrow [\ 2m\ (k^2/2m - h\Delta\omega\ )\ ]^{1/2}\ /\hbar = i\hbar^{-1}(2mh\Delta\omega)^{1/2}\left(1 - \frac{k^2}{2mh\Delta\omega}\right)^{1/2} \qquad [40b]$$

Thus in S_+ the wave number increases with $\Delta\omega$ and the photon energy $h\Delta\omega$ is absorbed into the translational energy. In S_- the wave number k' becomes *imaginary*.

Certain conclusions may now be drawn on the nature and relative contributions of the terms S_+ and S_- in the far wing region. In the near wing region these terms merge together into a single term where the dependence on $\Delta\omega$ is given solely through the function $[\Phi_a(\Delta\omega)+\Phi^*_b(-\Delta\omega)]$. On passing into the far wing region the nature of the two terms becomes quite different. Term S_+ continues to behave as a purely scattering function with scattering amplitudes corresponding to continuously increasing wave number: the photon energy $h\Delta\omega$ passing into the translational energy. In the term S_- we have to remember that we are dealing with elastic collisions and therefore the phase shifts are basically real. (The situation is more complicated for the corresponding part of the non-diagonal elements $M_{acdb}(\Delta\omega)$ which concerns inelastic collisions and the phase shifts are complex). With increasing $\Delta\omega$,

in the transition from the near wing to the far wing, the delta function decreases the wave number and puts the collision into a low energy regime where the phase shifts η_l are proportional (Ref. 14) to k^{2l+1}. When $h\Delta\omega = k^2/2m$, $k' = 0$ and the phase shift goes to zero. At this point, S_- is zero. Beyond this point the wave number and phase shift are imaginary. The appearance of imaginary phase shifts signifies a transition from a scattering process to one of absorption. For these reasons we can conclude that the functional dependence of $M_{aabb}(\Delta\omega)$ on $\Delta\omega$ changes dramatically in the transition region which will be marked by a turning point in the wing shape. A further conclusion is that the far line wings are normally asymmetric. This is because on the low frequency side, where $\Delta\omega$ is now negative, the roles of S_+ and S_- are interchanged: S_+ corresponding to absorption and S_- to scattering.

The analysis of the overlapping collision terms is more difficult in the absence of specific calculations. We can see however, that the two poles given by $[E_{k'}-E_k \pm h\Delta\omega]^{-1}$ which were near coincident in the near wing and thus cancelled out, now move in opposite directions: one towards infinite energy and the other towards zero energy. There will therefore be an increasing contribution from these terms as we move into the far wing region. The relative importance of this contribution is not evident.

Having established that there is a turning point near the transition region between the near and far wings of an isolated line, it would be useful to determine the direction of this feature, i.e., whether the far wing dips downwards or simply flattens out. An indication of this can found from the asymptotic limit of $M_{aabb}(\Delta\omega)$ as $\Delta\omega \to \infty$. This limit can be determined from eq. 36 as follows. First of all we take the asymptotic limits of $\Phi(\Delta\omega)$, $\Theta(\Delta\omega)$ and $\Psi(\Delta\omega)$, which are constants from eqs. 10c, 10d and 21, and neglect E_k compared with $h\Delta\omega$. Equation 36 then gives:

$$\lim_{\Delta\omega\to\infty} M_{aabb}(\Delta\omega) \to n_2\left\{-\frac{2\pi}{m}\left[\Phi_a(\infty)\,Ref_{aa}(0)-\Phi_b^*(-\infty)\,Ref_{bb}^*(0)\right] - \frac{iv}{2}\left[\Phi_a(\infty)\sigma_{aa}+\Phi_b^*(-\infty)\sigma_{bb}\right]\right.$$

$$\left. + \frac{i}{2m}\int dE d\Omega\; k\left(\delta[E-h\Delta\omega]\Phi_a(\infty)+\delta[E+h\Delta\omega]\Phi_b^*(-\infty)\right) f_{aa}(\Omega)\, f_{bb}^*(\Omega)\right.$$

$$- \frac{h\Delta\omega}{\pi m}\,\Theta(\infty)\int dE d\Omega\; k\left(\frac{P}{E^2-h^2\Delta\omega^2}\right) f^{*}_{aa}(\Omega) f_{bb}(\Omega)$$

$$- \frac{h\Delta\omega}{2\pi m}\,\Theta(\infty)\int dE\; E\; d\Omega\left(\frac{P}{E^2-h^2\Delta\omega^2}\right)\left(Q_{aa}(\Omega) f^{*}_{bb}(\Omega) + f_{aa}(\Omega) Q^{*}_{bb}(\Omega)\right)\Bigg\}_{AV} . \quad [41]$$

where the integrations over E are from 0 to ∞. The first two terms are constants. To evaluate the asymptotic limits of the remaining terms we can use approximations for the scattering amplitudes $f(\Omega,k)$ at low energies and high energies. The Born approximation (Ref. 14) can be used for the phase shift for large E ($= k^2/2m = k^2/2m\hbar^2$) → ∞. The first Born approximation gives $f(\Omega,k) \sim k^{-2}$ and the third term has components which fall off as $\Delta\omega^{-4}$ and therefore gives zero at $\Delta\omega = \infty$. Higher order Born approximations fall off even faster. The fourth and fifth terms can be written as

$$I_4 = - \underset{\Delta\omega\to\infty}{Lt} \frac{h\Delta\omega}{\pi m}\,\Theta(\infty)\int_0^{\infty} dE\; E^{1/2}\left(\frac{P}{E^2-h^2\Delta\omega^2}\right) F(\sqrt{E})$$

$$I_5 = - \underset{\Delta\omega\to\infty}{Lt} \frac{h\Delta\omega}{2\pi m}\,\Theta(\infty)\int_0^{\infty} dE\; E\left(\frac{P}{E^2-h^2\Delta\omega^2}\right) G(\sqrt{E})$$

At the upper limit, the functions $F(\sqrt{E})$ and $G(\sqrt{E})$ can be approximated using the first Born approximation where both converge. At the lower limit we can use a low energy approximation (Ref. 14) for the phase shift $\eta_l \sim k^{2l+1}$. With η_l small, as $k \to 0$, we have terms in l with $F(\sqrt{E}) \sim k^{4l}$ and $G(\sqrt{E}) \sim k^{4l-1}$. Again, both integrals are convergent at the lower limit.

There remains the problem of the pole at $E = h\Delta\omega$ in each integral. Since both integrals fall off rapidly in the regions of low and high energy we can expect that the main contribution to the integrals I_4 and I_5 will in fact come from the pole. However, since we are only interested in the limiting case $h\Delta\omega$ very large it is possible to approximate the functions $F(\sqrt{E})$ and $G(\sqrt{E})$ by their values at $E = h\Delta\omega$ and take them out of the integration. More exactly, we develop the functions about this value using a Taylor series expansion

$$F(\sqrt{E}) = F(\sqrt{h\Delta\omega}) + (\sqrt{E}-\sqrt{h\Delta\omega})F'(\sqrt{h\Delta\omega}) + (\sqrt{E}-\sqrt{h\Delta\omega})^2 F''(\sqrt{h\Delta\omega})/2 + \ldots.$$

Then, provided that the first and second derivatives exist and fall off with $h\Delta\omega$ faster than the $F(\sqrt{h\Delta\omega})$ we get an accurate approximation to the integral. These conditions are valid for both functions $F(\sqrt{h\Delta\omega})$ and $G(\sqrt{h\Delta\omega})$ using the first Born and higher approximations since, for example, $F(\sqrt{h\Delta\omega}) \sim (h\Delta\omega)^{-2}$. The principal values at the poles can now be evaluated as

$$I_4 \simeq - \underset{\Delta\omega\to\infty}{\mathrm{Lt}} \frac{h\Delta\omega}{\pi m} \Theta(\infty)\ F(\sqrt{h\Delta\omega})\ P_4, \quad \text{with} \quad P_4 = \underset{E\to\infty}{\mathrm{Lt}} \int_{E-e}^{E+e} dE\ E^{1/2} \left(\frac{1}{E^2 - h^2\Delta\omega^2} \right),$$

$$I_5 \simeq - \underset{\Delta\omega\to\infty}{\mathrm{Lt}} \frac{h\Delta\omega}{2\pi m} \Theta(\infty)\ G(\sqrt{h\Delta\omega})\ P_5, \quad \text{with} \quad P_5 = \underset{E\to\infty}{\mathrm{Lt}} \int_{E-e}^{E+e} dE\ E \left(\frac{1}{E^2 - h^2\Delta\omega^2} \right),$$

and the limit $e \to 0$ is to be taken after the limit $E \to \infty$. We obtain

$$P_4 = \underset{E\to\infty}{\mathrm{Lt}} \frac{1}{\sqrt{h\Delta\omega}} \left\{ \frac{1}{2} \log \left| \frac{\sqrt{h\Delta\omega}+\sqrt{(E+e)}}{\sqrt{h\Delta\omega}-\sqrt{(E+e)}} \right| - \frac{1}{2} \log \left| \frac{\sqrt{h\Delta\omega}+\sqrt{(E-e)}}{\sqrt{h\Delta\omega}-\sqrt{(E-e)}} \right| \right.$$
$$\left. - \tan^{-1} \left(\frac{E+e}{h\Delta\omega} \right)^{1/2} + \tan^{-1} \left(\frac{E-e}{h\Delta\omega} \right)^{1/2} \right\} = 0,$$

$$P_5 = \underset{E\to\infty}{\mathrm{Lt}} \frac{1}{2} \left\{ \log \left| (E+e)^2 - (h\Delta\omega)^2 \right| - \log \left| (E-e)^2 - (h\Delta\omega)^2 \right| \right\} = 0.$$

The fourth and fifth terms are therefore also zero and eq. (41) becomes

$$M(\infty)_{aabb} = n_2 \left\{ - \frac{2\pi}{m} \left[\frac{\mathcal{T}_a}{\bar{T}_a} Re\ f_{aa}(0) - \frac{\mathcal{T}_b^*}{\bar{T}_b^*} Re\ f_{bb}^*(0) \right] \right.$$
$$\left. - \frac{iv}{2} \left[\frac{\mathcal{T}_a}{\bar{T}_a} \sigma_{aa} + \frac{\mathcal{T}_b^*}{\bar{T}_b^*} \sigma_{bb} \right] \right\}_{AV}. \quad [42]$$

where we have used the asymptotic expressions of eqs. 10c and 10d. Thus, the real and imaginary parts of $M(\infty)_{aabb}$ converge to constants which are simple functions of the elementary collisional constituents $f(0)$ and the collision times. A good approximation to the right-hand side of eq. 42 can be easily obtained. Thus, assuming that all the parameters in the two states are approximately equal, the first term is small and can be neglected and we have

$$M^{(\infty)}_{aabb} \simeq - in_2 \left\{ v \left[\frac{\mathcal{T}_a}{\bar{T}_a} \sigma_{aa} + \frac{\mathcal{T}^*_b}{\bar{T}^*_b} \sigma_{bb} \right] \right\}_{AV} \simeq - in_2 \left\{ v\sigma \left[\frac{\mathcal{T}_a}{\bar{T}_a} + \frac{\mathcal{T}^*_b}{\bar{T}^*_b} \right] \right\}_{AV},$$

assuming that $\sigma_{aa} \simeq \sigma_{bb} \simeq \sigma$. The average of $n_2 v\sigma$ can be identified with the collision frequency Γ_k, of the kinetic theory of gases, giving

$$M^{(\infty)}_{aabb} \simeq - i\Gamma_k \left[\frac{\mathcal{T}_a}{\bar{T}_a} + \frac{\mathcal{T}^*_b}{\bar{T}^*_b} \right]. \qquad [42a]$$

The theory predicts that after the turning point near the transition region the real and parts of $M^{(\infty)}_{aabb}$ tend towards constant values. This results in a Voigt profile for the far line wing. To see this we write

$$M^{(\omega)}_{aabb} = \Delta^{(\omega)}_{aabb} - i\Gamma^{(\omega)}_{aabb}$$

and the absorption coefficient for an isolated infrared line (of Doppler width σ_D) in the far wing is given by

$$\alpha(\omega) \sim n_1 \pi^{-3/2} S\, \omega \tanh(\beta h\omega/2) \int_{-\infty}^{\infty} dt\, e^{-t^2} \frac{\Gamma(\infty)}{[\Delta\omega - \Delta(\infty) - \sigma_D t]^2 + \Gamma(\infty)^2}, \qquad [43]$$

where $\Gamma(\infty) \simeq \Gamma_k\, Re \left[\frac{\mathcal{T}_a}{\bar{T}_a} + \frac{\mathcal{T}^*_b}{\bar{T}^*_b} \right]$, $\Delta(\infty) \simeq \Gamma_k\, Im \left[\frac{\mathcal{T}_a}{\bar{T}_a} + \frac{\mathcal{T}^*_b}{\bar{T}^*_b} \right]$.

Some experimental corroboration is available for this result. In Part II we applied the near wing theory to the continuum beyond the band head of the ν_3 band of CO_2 near 4.2 μm. As discussed in Part II the experimental results of Cann et al. (Ref.15) were used for CO_2 broadened by N_2 at a temperature of 296K. Reference 15 also gives reults for O_2 and self-broadening. These results are in the form of a form factor $\chi(\Delta\omega)$ which, for $\Delta\omega > 50$ cm^{-1}, is basically equivalent to $\Gamma(\omega)$ (as discussed in Part II). Cann et al. determined $\chi(\Delta\omega)$ empirically by an inversion of the continuum absorption assuming that the same $\chi(\Delta\omega)$ was valid for each line in the CO_2 band. This form factor is plotted in Fig. 1 for self and N_2 broadening (O_2 and N_2 are

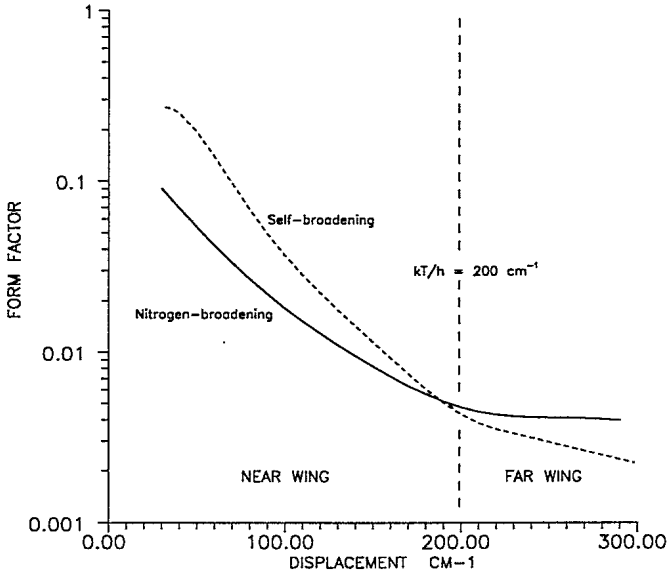

FIGURE 1 - Form factors for self- and foreign-gas broadening of CO_2 (Ref. 15)

near identical). In each case, the predicted turning point is seen near $\Delta\omega$ = 200 cm^{-1} and the $\chi(\Delta\omega)$ then levels off towards a constant value. In the case of CO_2 broadened by N_2, this value is about 0.004. This result can be used in conjunction with those of Part II where, applying the near wing approximation eq. 37 to the experimental data of Cann et al., estimates were obtained for the real and imaginary parts of T_{aa} and T_{bb} by inversion (assuming that $\mathcal{T} << T$). We obtained $Re\ (T_{aa},T_{bb}) \simeq 24,\ 27 \times 10^{-13}$s and $Im\ (T_{aa},T_{bb}) \simeq 8,\ 7 \times 10^{-13}$s. Taking $\Gamma_k \simeq 0.04\ cm^{-1}$ and an average half width $\Gamma(0)_{aabb} \simeq 0.07\ cm^{-1}$, and assuming the same relative proportions for the real and imaginary parts of $\mathcal{T}$ as for T, we find that the free propagation times $\mathcal{T}$ are smaller than the collision times T by a factor $\simeq 7 \times 10^{-3}$. This result also justifies the approximation of Part II that, in the near wing approximation, we can neglect $\mathcal{T}$ in comparison with T in the spectral distribution functions Φ.

6.0 DISCUSSION AND CONCLUSIONS

The collision time theory allows a considerable simplification of the number and form of the terms contributing to the matrix elements of Fano's relaxation operator, particularly for the diagonal elements $M_{aabb}(\omega)$. The

analysis of the diagonal terms and their application to an isolated line wing shows that the latter is composed of two regions of different functional behaviour: the near and far wing regions. The demarcation between the two regions occurs near a displacement from the line centre $\Delta\omega \sim kT/h$. In the near wing the collision parameters are essentially those of the impact approximation and the shape of this part of the wing is determined by the rapidly changing spectral distribution functions $\Phi_a(\Delta\omega)$ and $\Phi_b^*(-\Delta\omega)$. Near the transition region, between the near and far wings, several changes occur. The singular contributions, S_+ and S_-, which were merged together in the near wing, begin to behave divergently: S_+ continuing to behave as a scattering function and S_- becoming an absorption function. At the same time, the collision overlap terms cease to cancel out mutually and become non-negligible. The shape of the far wing is largely determined by the nature and specific details of the binary molecular interactions. This is because although the spectral distribution functions $\Phi_a(\Delta\omega)$, $\Phi_b^*(-\Delta\omega)$, $\Theta(\Delta\omega)$ and $\Psi(\Delta\omega)$ exhibit significant variations at small values of Δw, in the far wing they tend to level out to constant values.

All theories of line shape must obey the Nyquist relation

$$\frac{1}{2}\int_{-\infty}^{\infty} d\omega \frac{\chi''(\omega)}{\tanh(\beta h\omega/2)} = n_1 \sum_{ab} S_{ab},$$

where $\chi''(\omega)$ is the imaginary part of the susceptibility and S_{ab} is the line strength. This condition is very important because it ensures that the integrated band intensity is unaltered by a redistribution of line intensity, due to line coupling effects and strong deviations of individual line wings from the Lorentz form. Now, it does not appear possible to prove with complete mathematical rigour that the theory obeys the Nyquist relation. This is because the expressions for the frequency dependence of the relaxation matrix $M_{acdb}(\Delta\omega)$ are too complicated for analytical evaluation in the integration. However, it is fairly easy, using asymptotic properties that we have derived for $M_{acdb}(\Delta\omega)$, to carry out a good analytic approximation of the Nyquist integral to show that it tends towards the desired result. This analysis is carried out in Appendix B, where it is evident that the main reason that integral tends towards the Nyquist condition is due to the nature

of the line coupling mechanism derived in Part I.

Another test of the validity of the theory is the proper convergence of moment integrals*. Thus, the moments of the real part of the complex susceptibility $\chi(\omega)$ must be finite and the question arises whether this is true in the present case, where the asymptotic limits of the line wing behave as Voigt profiles, eq. 43. This is demonstrated in Appendix C.

Whilst the collision time theory provides a considerable reduction of Fano's relaxation matrix and enables a better understanding of the significance of the various terms, entirely theoretical calculations are still extremely difficult, especially for molecular interactions. For the near wing, assuming impact parameters are already available, it is necessary to calculate the collision times T and $\mathcal{T}$ (diagonal elements). In the far wing we also have to perform new types of calculations to take into account the collisional absorption and overlapping binary effects.

In terms of extracting collision interaction information from experimental line wing results by inversion, the near wing yields estimates only of the collision time T. Information about the relative magnitude of the free propagation time $\mathcal{T}$, compared with T, can be obtained from the asymptotic far line wing.

In the absence of specific calculations, direct comparison with other theories is not yet possible. A comparison with Rosenkranz's quasistatic theory (Ref. 8) and its further development (Refs. 9 and 10) would be particularly interesting. This is because it applies to the same far wing region but is based on diametrically opposed concepts and assumptions. Thus, a basic premise of quasistatic theories is that the collision times are infinite and the statistical distribution can be treated as though the molecules were stationary. The theory is therefore
primarily applicable to the asymptotic far wing. However, very recently Ma and Tipping (Ref. 16) have further developed the quasistatic theory to include corrections for the near wing and molecular motion.

* Private communication: Prof. C. Boulet, 1994.

In contrast, the collision time theory used in this report and in Part II is very different in concept to the quasistatic theory. The key issue is that the theory is developed strictly in the frequency domain where the Fano relaxation operator is defined. In this domain, "times" appear as constants or parameters and not variables. The principal variable is frequency in the form of a quantum of energy $h\Delta\omega$. This is borne out by the collision time theory which relates deviations off the energy shell of the transition matrix to collision times which are fixed calculable quantities. As Fano noted (Ref. 1) the variation of the transition operator $t(E)$ as a function of its energy argument E is a measure of the duration of a collision. The collision times which arise out of the collision time theory do so through a quantum mechanical time *operator* $-ih\partial/\partial E$ (see II). The collision duration time T is therefore a quantum mechanical quantity with the dimensions of time. Its matrix elements do not have an exact classical counterpart: T is, in fact, complex. Similarly, when we refer to the free propagator time operator $\mathcal{T}$ (defined by eq. 12) as the time a molecular pair would spend in the same vicinity in the absence of the interaction, this is only true in a quantum mechanical sense. $\mathcal{T}$ is, in fact, merely a convenient form in which to express the free propagator $(E-H_o)^{-1}$: it has no classical counterpart and, like T, is complex.

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APPENDIX A

Evaluation of some Principal Value Integrals

Consider first the integral I_1:

$$\pi i I_1 = \int_{-\infty}^{\infty} d\psi \; \frac{P}{\psi-\varepsilon_c-E_{k'}} \; \Phi_c(\psi-\varepsilon_c-E_{k'}) \; \Phi_d^*(\psi-\varepsilon_d-E_{k'}-h\Delta\omega_{cd})$$

$$= \int_{-\infty}^{\infty} d\psi \; \frac{P}{\psi-\varepsilon_c-E_{k'}} \left(1+\frac{i(T_c/h)(\psi-\varepsilon_c-E_{k'})}{1-i(\bar{T}_c/h)(\psi-\varepsilon_c-E_{k'})}\right)\left(1-\frac{i(T_d^*/h)(\psi-\varepsilon_c-E_{k'}-h\Delta\omega_{cd})}{1+i(\bar{T}_d^*/h)(\psi-\varepsilon_c-E_{k'}-h\Delta\omega_{cd})}\right). \qquad [A1]$$

Defining the complex parameters

$$A = T_c/\bar{T}_c, \quad B = h/\bar{T}_c, \quad C = T_d^*/\bar{T}_d^*, \quad D = h/\bar{T}_d^*,$$

and putting $\Delta = h\Delta\omega_{cd}$, $x = \varepsilon_c+E_{k'}$, I_1 can be written

$$\pi i I_1 = \int_{-\infty}^{\infty} d\psi \; \frac{P}{\psi-x}\left(1-\frac{A(\psi-x)}{\psi-x+iB}\right)\left(1-\frac{C(\psi-x-\Delta)}{\psi-x-\Delta-iD}\right)$$

$$= \int_{-\infty}^{\infty} d\psi \left(\left[1-C+\frac{iCD}{\Delta+iD}\right]\frac{P}{\psi-x} - \left[A(1-C)+\frac{iACD}{\Delta+i(B+D)}\right]\frac{1}{\psi-x+iB} + \left[-\frac{iCD}{\Delta+iD}+\frac{iACD}{\Delta+i(B+D)}\right]\frac{1}{\psi-x-\Delta-iD}\right)$$

$$= \int_{-\infty}^{\infty} d\psi \left(-\left[A(1-C)+\frac{iACD}{\Delta+i(B+D)}\right]\frac{1}{\psi-x+iB} + \left[-\frac{iCD}{\Delta+iD}+\frac{iACD}{\Delta+i(B+D)}\right]\frac{1}{\psi-x-\Delta-iD}\right), \qquad [A2]$$

where we have used $\int_{-\infty}^{\infty} d\psi \; \frac{P}{\psi-x} = 0$. Changing the variables in the remaining integrals (which are not principal values)

$$\pi i I_1 = \int_{-\infty}^{\infty} dt \left\{ -\left[A(1-C)+\frac{iACD}{\Delta+i(B+D)}\right]\frac{1}{t+iB} + \left[-\frac{iCD}{\Delta+iD}+\frac{iACD}{\Delta+i(B+D)}\right]\frac{1}{t-iD}\right\}. \qquad [A3]$$

Now, B ~ a+ib and D ~ c-id, whence integrals are, for *Re* p > 0, of form

$$I = \int_{-\infty}^{\infty} dt \; \frac{1}{t\pm ip} = \int_{-\infty}^{\infty} dt \; \frac{t\mp ip}{t^2+p^2} = \mp 2ip \int_0^{\infty} dt \; \frac{1}{t^2+p^2} = \mp 2ip \left[\frac{1}{p}\tan^{-1}\frac{t}{p}\right]_0^{\infty} = \mp\pi i.$$

Whence, eq. A3 becomes

$$I_1 = \left[A(1-C)+\frac{iACD}{\Delta+i(B+D)}\right]+\left[-\frac{iCD}{\Delta+iD}+\frac{iACD}{\Delta+i(B+D)}\right] = A(1-C)+\frac{2iACD}{\Delta+i(B+D)}-\frac{iCD}{\Delta+iD}. \quad [A4]$$

However, the last term of eq. A4 is related to $\Phi_d^*(-\Delta\omega_{cd})$,

i.e. $$\frac{iCD}{\Delta+iD} = \frac{C[(\Delta+iD)-\Delta]}{\Delta+iD} = C - \frac{C\Delta}{\Delta+iD} = C + \Phi_d^*(-\Delta\omega_{cd}) - 1,$$

whence $$I_1 = (1+A)(1-C) + \frac{2iACD}{\Delta+i(D+B)} - \Phi_d^*(-\Delta\omega_{cd}). \quad [A5]$$

It follows that I_2 is the same as I_1 with $h\Delta\omega_{cd}$ replaced by $h\Delta\omega_{ab}$.

In an exactly similar fashion I_3 and I_4 follow. Thus, we obtain:

$$I_3 = -\left[(1+C)(1-A) + \frac{2iABC}{\Delta+i(B+D)}\right] + \Phi_c(\Delta\omega_{cd}). \quad [A6]$$

It is now convenient to define two new spectral distributions:

$$\Theta_{cd}(\Delta\omega_{cd}) = (1+A)(1-C)/2 + \frac{iACD}{\Delta+i(B+D)} - \Phi_d^*(-\Delta\omega_{cd})$$

$$= (1+T_c/\bar{T}_c)(1-T_d^*/\bar{T}_d^*)/2 + \frac{(T_c T_d^*/\bar{T}_d^*)}{(\bar{T}_d^*+\bar{T}_c)-i\bar{T}_c\bar{T}_d^*\Delta\omega_{cd}} - \Phi_d^*(-\Delta\omega_{cd}), \quad [A7]$$

$$\Psi_{cd}(\Delta\omega_{cd}) = (1+C)(1-A)/2 + \frac{iABC}{\Delta+i(B+D)} - \Phi_c(\Delta\omega_{cd})$$

$$= (1-T_c/\bar{T}_c)(1+T_d^*/\bar{T}_d^*)/2 + \frac{(T_c T_d^*/\bar{T}_c)}{(\bar{T}_d^*+\bar{T}_c)-i\bar{T}_c\bar{T}_d^*\Delta\omega_{cd}} - \Phi_c(\Delta\omega_{cd}). \quad [A8]$$

Then $I_1 = 2\Theta_{cd}(\Delta\omega_{cd}) + \Phi_d^*(-\Delta\omega_{cd})$; $I_2 = 2\Theta_{cd}(\Delta\omega_{ab}) + \Phi_b^*(-\Delta\omega_{ab})$

$I_3 = -[2\Psi_{cd}(\Delta\omega_{cd}) + \Phi_c(\Delta\omega_{cd})]$; $I_4 = -[2\Psi_{cd}(\Delta\omega_{ab}) + \Phi_a(\Delta\omega_{ab})]$

APPENDIX B

Approximate Evaluation of the Nyquist Relation

We wish to show that the theory conforms to the Nyquist relation

$$\frac{1}{2}\int_{-\infty}^{\infty} d\omega \frac{\chi''(\omega)}{\tanh(\beta h\omega/2)} = n_1 \sum_{ab} S_{ab}. \qquad [B1]$$

In Part I it was shown that the integral on the LHS is basically

$$I = \frac{1}{2}\int_{-\infty}^{\infty} d\omega \frac{\chi''(\omega)}{\tanh(\beta h\omega/2)} = n_1 \frac{1}{2}\sum_{ab} S_{ab}\int_{-\infty}^{\infty} d\omega\ [F_{ab}(\omega) + F_{ab}(-\omega)], \qquad [B2]$$

where, for simplicity, we have neglected the Doppler width. This approximation does not effect the discussion and can be readily omitted. The function $F(\omega)$ is given by eq. 38 of Part I:

$$F_{ab}(\omega) = \frac{1}{\pi}\left\{ \frac{\Gamma_{aabb}(\omega)[1+P_{ab}(\omega)]+[\omega-\omega_{ab}-\Delta_{aabb}(\omega)]Q_{ab}(\omega)}{[\omega-\omega_{ab}-\Delta_{aabb}(\omega)]^2+\Gamma^2_{aabb}(\omega)} \right.$$

$$\left. - \sum_{\substack{c\neq a\\ d\neq b}} \frac{\Gamma_{ccdd}(\omega)H_{acdb}(\omega)+[\omega-\omega_{cd}-\Delta_{ccdd}(\omega)]J_{acdb}(\omega)}{[\omega-\omega_{cd}-\Delta_{ccdd}(\omega)]^2+\Gamma^2_{ccdd}(\omega)} \right\}. \qquad [B3]$$

where

$$P_{ab}(\omega) = \sum_{\substack{c\neq a\\ d\neq b}} \frac{\mu_{ab}S_{cd}}{\mu_{cd}S_{ab}} A_{acdb}(\omega), \quad [B4a]; \qquad Q_{ab}(\omega) = \sum_{\substack{c\neq a\\ d\neq b}} \frac{\mu_{ab}S_{cd}}{\mu_{cd}S_{ab}} B_{acdb}(\omega), \qquad [B4b]$$

$$H_{acdb}(\omega) = \frac{\mu_{ab}S_{cd}}{\mu_{cd}S_{ab}} A_{acdb}(\omega), \quad [B5a]; \qquad J_{acdb}(\omega) = \frac{\mu_{ab}S_{cd}}{\mu_{cd}S_{ab}} B_{acdb}(\omega). \qquad [B5b]$$

and
$$A_{acdb}(\omega) = \frac{[\Delta_{acdb}(\omega)(\omega_{ab}-\omega_{cd}-\Delta_{ccdd}(\omega)+\Delta_{aabb}(\omega))-\Gamma_{acdb}(\omega)(\Gamma_{ccdd}(\omega)-\Gamma_{aabb}(\omega))]}{(\omega_{ab}-\omega_{cd}-\Delta_{ccdd}(\omega)+\Delta_{aabb}(\omega))^2+(\Gamma_{ccdd}(\omega)-\Gamma_{aabb}(\omega))^2}, \qquad [B6]$$

$$B_{acdb}(\omega) = \frac{[\Gamma_{acdb}(\omega)(\omega_{ab}-\omega_{cd}-\Delta_{ccdd}(\omega)+\Delta_{aabb}(\omega))+\Delta_{acdb}(\omega)(\Gamma_{ccdd}(\omega)-\Gamma_{aabb}(\omega))]}{(\omega_{ab}-\omega_{cd}-\Delta_{ccdd}(\omega)+\Delta_{aabb}(\omega))^2+(\Gamma_{ccdd}(\omega)-\Gamma_{aabb}(\omega))^2}. \qquad [B7]$$

(Note that in eqs. B3 - B4 we have retained the notation of Part I for the arguments of Δ and Γ, i.e. $\Delta(\omega)$ rather than $\Delta(\Delta\omega)$ which was adopted in the present paper). $P_{ab}(\omega)$ and $Q_{ab}(\omega)$, and the $H_{acdb}(\omega)$ and $J_{acdb}(\omega)$, are coupling "coefficients" and would be constants were it not for their frequency dependence on such quantities as $\Delta_{aabb}(\pm\omega)$ and $\Gamma_{aabb}(\pm\omega)$ etc. We consider the first term in eq. B2, i.e., the positive resonance term $F(\omega)$. The negative resonance term can be evaluated in an identical manner. Making use of the relations between the coupling coefficients, namely

$$P_{ab}(\omega) = \sum_{\substack{c\neq a \\ d\neq b}} H_{acdb}(\omega) \quad , \text{ and } \quad Q_{ab}(\omega) = \sum_{\substack{c\neq a \\ d\neq b}} J_{acdb}(\omega),$$

it is convenient to write the integral in the form

$$I_1 = n_1 \frac{1}{2} \sum_{ab} S_{ab} \int_{-\infty}^{\infty} d\omega \; F_{ab}(\omega)$$

$$= n_1 \frac{1}{2\pi} \sum_{ab} S_{ab} \int_{-\infty}^{\infty} d\omega \left\{ \frac{\Gamma_{aabb}(\omega)}{[\omega - \omega_{ab} - \Delta_{aabb}(\omega)]^2 + \Gamma^2_{aabb}(\omega)} \right.$$

$$+ \sum_{\substack{c\neq a \\ d\neq b}} \left[H_{acdb}(\omega) \left(\frac{\Gamma_{aabb}(\omega)}{[\omega - \omega_{ab} - \Delta_{aabb}(\omega)]^2 + \Gamma^2_{aabb}(\omega)} - \frac{\Gamma_{ccdd}(\omega)}{[\omega - \omega_{cd} - \Delta_{ccdd}(\omega)]^2 + \Gamma^2_{ccdd}(\omega)} \right) \right.$$

$$\left. \left. + J_{acdb}(\omega) \left(\frac{[\omega - \omega_{ab} - \Delta_{aabb}(\omega)]}{[\omega - \omega_{ab} - \Delta_{aabb}(\omega)]^2 + \Gamma^2_{aabb}(\omega)} - \frac{[\omega - \omega_{cd} - \Delta_{ccdd}(\omega)]}{[\omega - \omega_{cd} - \Delta_{ccdd}(\omega)]^2 + \Gamma^2_{ccdd}(\omega)} \right) \right] \right\}. \qquad [B8]$$

First of all, from the asymptotic properties of the diagonal and non-diagonal elements of $\Delta(\omega)$ and $\Gamma(\omega)$ derived in this paper as $\omega \to \infty$, it is evident that the integral converges. Thus the diagonal elements tend to small constants and the non-diagonal elements tend to zero.

In order to carry out an approximate evaluation of the integral the only latitude we have is to replace the diagonal elements $\Gamma_{aabb}(\omega)$ and $\Delta_{aabb}(\omega)$ and the non-diagonal elements $\Gamma_{acdb}(\omega)$ and $\Delta_{acdb}(\omega)$ by constant values such that I_1 is dominated by the contributions at these values. In fact, as we shall see, we need only to make appropriate choices for the diagonal elements $\Gamma_{aabb}(\omega)$ and $\Delta_{aabb}(\omega)$. Consider first the first term of eq. B8. From the present paper and

Part II we know that $\Gamma(\omega)_{aabb}$ has a peak value at the line centre which is its impact approximation limit $\Gamma(0)_{aabb}$, so this is the value we choose. It can therefore be taken out of the integral. $\Delta(\omega)_{aabb}$, on the other hand, is small at the line centre, but exhibits a maximum and a minimum on either side (see Part II). The contributions from the maximum and minimum balance out under the integration, so it is a good approximation to replace $\Delta(\omega)_{aabb}$ by $\Delta(0)_{aabb}$. The same approximations are also made for the same functional components in the remaining terms of eq. B8. The $\Delta(\omega)$ and $\Gamma(\omega)$ may manifest satellite line maxima arising from any low energy resonances in the scattering amplitudes, however these secondary maxima, if they occur, must be very small and we can assume that they contribute little to the integrand.

There remains the question of determining the appropriate approximate values for the coefficients $H(\omega)_{acdb}$ and $J(\omega)_{acdb}$. Since these depend entirely on all the diagonal and non-diagonal elements through $A(\omega)_{acdb}$ and $B(\omega)_{acdb}$ of eqs. B6 and B7 a reasonable choice would be to use the impact approximation values to obtain values $H(0)_{acdb}$ and $J(0)_{acdb}$. Substituting these values in eq. B8 we obtain an integral which can be readily evaluated:

$$I_1 \simeq n_1 \frac{1}{2\pi} \sum_{ab} S_{ab} \int_{-\infty}^{\infty} d\omega \left\{ \frac{\Gamma(0)_{aabb}}{[\omega - \omega_{ab} - \Delta(0)_{aabb}]^2 + \Gamma^2(0)_{aabb}} \right.$$

$$+ \sum_{\substack{c\neq a \\ d\neq b}} \left[H(0)_{acdb} \left(\frac{\Gamma(0)_{aabb}}{[\omega - \omega_{ab} - \Delta(0)_{aabb}]^2 + \Gamma^2(0)_{aabb}} - \frac{\Gamma(0)_{ccdd}}{[\omega - \omega_{cd} - \Delta(0)_{ccdd}]^2 + \Gamma^2(0)_{ccdd}} \right) \right.$$

$$\left. \left. + J(0)_{acdb} \left(\frac{[\omega - \omega_{ab} - \Delta(0)_{aabb}]}{[\omega - \omega_{ab} - \Delta(0)_{aabb}]^2 + \Gamma^2(0)_{aabb}} - \frac{[\omega - \omega_{cd} - \Delta(0)_{ccdd}]}{[\omega - \omega_{cd} - \Delta(0)_{ccdd}]^2 + \Gamma^2(0)_{ccdd}} \right) \right] \right\}$$

$$\simeq n_1 \frac{1}{2\pi} \sum_{ab} S_{ab} \left\{ \pi + \sum_{\substack{c\neq a \\ d\neq b}} \left[H(0)_{acdb} \left(\pi - \pi \right) + J(0)_{acdb} \left(\infty - \infty \right) \right] \right\} \simeq n_1 \frac{1}{2} \sum_{a} S_{ab}. \qquad [B9]$$

The same result is obtained from the negative resonance term and the Nyquist is therefore valid to a good approximation. Equation B9 shows that it matters little what "reasonable" approximation is used for $H(\omega)_{acdb}$ and $J(\omega)_{acdb}$, since the terms associated with these cancel out. This is due to the form of the line coupling mechanism which causes the gain and loss coupling terms

tend to cancel out over the overall band intensity.

APPENDIX C

Moments of the Susceptibility in the Far Wing Asymptotic Limit

We wish to show that the moments of the real part of the complex susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$, are finite. The response function $\phi_{\mu\mu}(t)$ and $\chi(\omega)$ are related by the following expression (see Part I, eq. 20)

$$\chi(\omega) = \int_0^\infty d\tau\ e^{-i\omega t}\ \phi_{\mu\mu}(t), \qquad [C1]$$

from which, by inversion and successive time derivatives (see for example Kubo, Ref.17), the moments are defined by

$$(-1)^m\ \phi_{\mu\mu}^{(2m)}\ (0) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega\ \omega^{2m}\chi''(\omega). \qquad [C2]$$

The imaginary part of the susceptibility (see eqs. 34 - 38 of Part II) is

$$\chi''(\omega) = \frac{n_1\ c\ \tanh(\beta h\omega/2)}{8\pi^{7/2}} \sum_{ab} S_{ab} \int_{-\infty}^{\infty} dt\ e^{-t^2}\ [F_{ab}(\omega) + F_{ab}(-\omega)]. \qquad [C3]$$

Retaining only the positive resonance term $F(\omega)$, and in particular the isolated line (neglecting line coupling effects), we are concerned, in the evaluation of the moments Eq. C2, with integrals of the form:

$$I_m = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega\ \omega^{2m}\ \tanh(\beta h\omega/2) \int_{-\infty}^{\infty} dt\ e^{-t^2}\ \frac{\Gamma(\omega)}{[\omega-\omega_o-\Delta(\omega)-\sigma\ t]^2 + \Gamma^2(\omega)}$$

$$= \int_{-\infty}^{\infty} d\omega\ \omega^{2m}\ \tanh(\beta h\omega/2)\ U(x,y). \qquad [C4]$$

where U(x,y) is the real part of the complex error function and the variables are

$$x = [\omega - \omega_o - \Delta(\omega)]/\sigma_D, \quad y = \Gamma(\omega)/\sigma_D, \quad \sigma_D = \text{Doppler width.}$$

The problem is to show that the integrand (which is an odd function due to the $\tanh(\beta h\omega/2)$ function which is odd) of eq. C4 is finite at the limits $\omega \to \pm\infty$ where, as we have shown, $\Gamma(\infty)$ and $\Delta(\infty)$ tend to constants Γ and Δ in the asymptotic far wing. This is readily evident using an asymptotic expansion for the function U(x,y) derived by Reichel, Ref. 18:

$$U(x,y) = \frac{1}{\pi^{1/2} y} e^{-x^2} \sum_{n=o}^{\infty} \frac{x^{2n}}{n!} S_n,$$

The coefficients $S_n(y)$ are functions of y only and obey the recurrence relation

$$S_n = \frac{2y^2}{(2n-1)} (1-S_{n-1}), \qquad \text{where } S_o = \pi^{1/2} y\, e^{y^2} \operatorname{erfc} y.$$

In the limit $\omega,\ x \to \pm\infty$ the integrand of eq. C4

$$\omega^{2m} \tanh(\beta h\omega/2)\ U(x,y) \to \pm \frac{x^{2m}}{\pi^{1/2} y} e^{-x^2} \sum_{n=o}^{\infty} \frac{x^{2n}}{n!} S_n \to 0,$$

because of the exponential factor. The line coupling terms in $F(\omega)$ contain the imaginary part V(x,y) of the complex error function, and one can use Reichel's form

$$V(x,y) = \frac{x}{\pi^{1/2} y^2} e^{-x^2} \sum_{n=o}^{\infty} \frac{x^{2n}}{n!} S_{n+1}$$

to show that their contribution to the moments is also finite.

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